Three-dimensional flower-like $ZnIn_2S_4$/NiO/ZIF-67 hierarchical spheres for enhanced visible-light photocatalytic hydrogen evolution

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DFT calculations detail

The density functional theory (DFT) calculation was carried out using the Cambridge serial total energy package (CASTEP) code, in which a plane wave basis set was used. The model was established by the generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof (PBE) functional. The cutoff energy of the OTFG ultrasoft pseudopotential was 571.40 eV. The Brillouin zone integration was performed using 3×2×1 k-point sampling through all the computational process. Geometric convergence tolerances with maximum force and maximum displacement were 0.03 eV/Å and 10^{-3}Å. Self-consistent field (SCF) tolerance with high accuracy of 10^{-6} eV/atom for energy convergence. The d band center (ε) was calculated based on the following equation: where ρ(x) is the PDOS at the energy of x. The detailed information about the structural model used in the DFT calculations as follow:

$$\varepsilon = \frac{\int_{-\infty}^{\infty} \rho(x) x dx}{\int_{-\infty}^{\infty} \rho(x) dx}$$

Where ρ(x) is the PDOS at the energy of x.

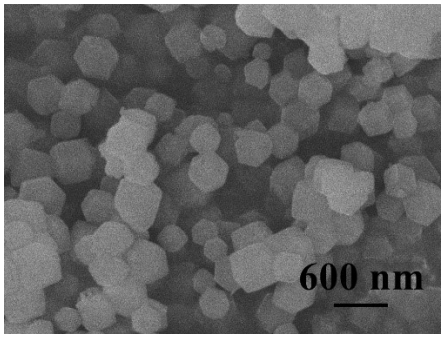

Fig S1. SEM image of the ZIF-67

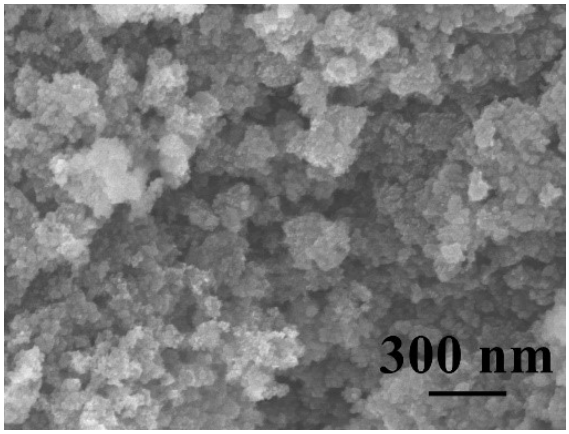

Fig S2. SEM image of the NiO/ZIF-67

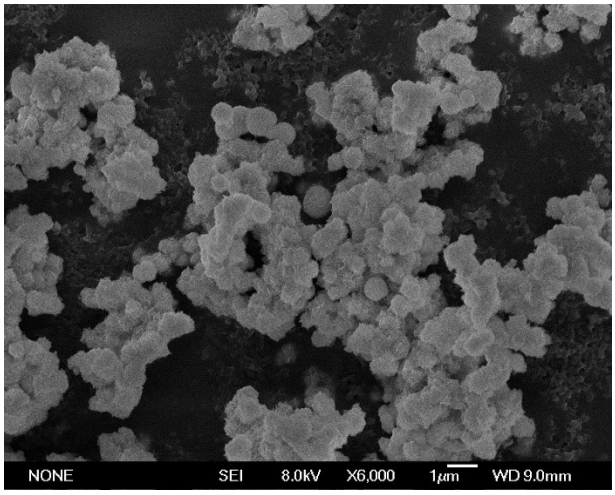

Fig S3. The original SEM image of NiO/ZIF-67 in Fig 2c.

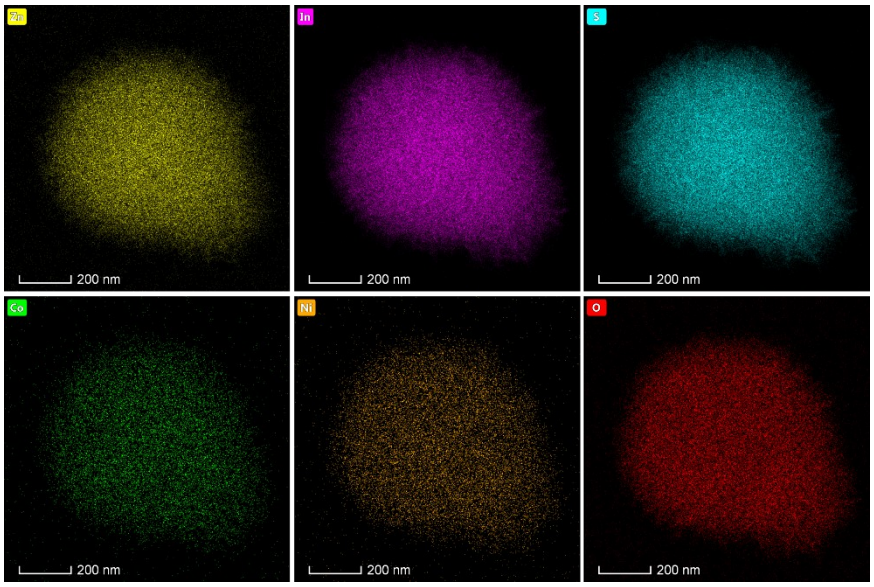

Fig S4. The original elemental mapping analysis of Zn, In, S, Co, Ni and O in ZIS/NiO/ZIF-67.

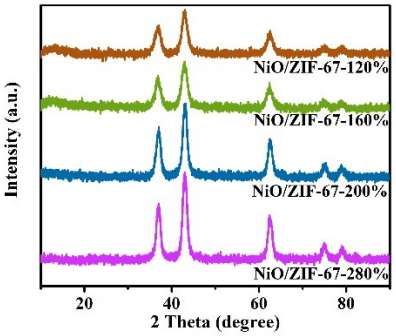

Fig S5. XRD patterns of NiO/ZIF-67-120%, NiO/ZIF-67-160%, NiO/ZIF-67-200% and NiO/ZIF-67-280%.

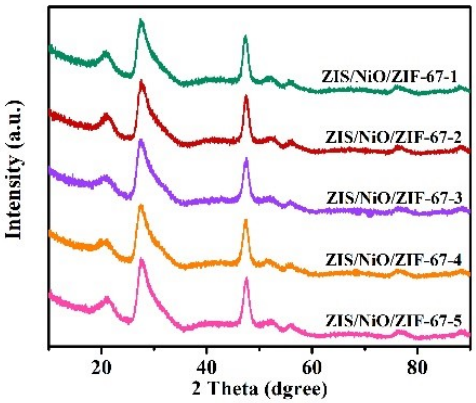

Fig S6. XRD patterns of ZIS/NiO/ZIF-67.

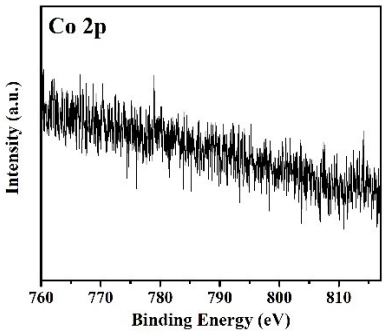

Fig. S7. The XPS spectral of Co 2p.

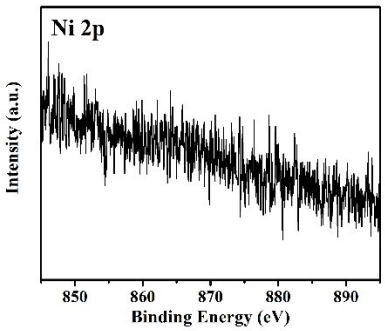

Fig S8. The XPS spectral of Ni 2p.

Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
8	O	K	11.27	1.79	3.31	0.29	2.46
16	S	K	52.30	12.74	30.75	6.28	0.80
27	Co	K	0.26	0.05	0.29	0.05	1.87
28	Ni	K	0.90	0.19	0.97	0.15	0.81
30	Zn	K	10.54	2.17	12.64	1.99	0.08
49	In	L	24.72	4.79	52.05	7.36	0.12

Table S1. The element content analysis of ZIS/NiO/ZIF-67.